Benzoyl peroxide oxidation route to polyaniline salt and its use as catalyst in tetrahydropyranylation of decanol

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In this work, benzoyl peroxide is used as an oxidizing agent to oxidize aniline to polyaniline salt in the presence of protic acids such as sulfuric or nitric acid. The polymer samples are characterized by infrared, X-ray diffraction, particle size, resistance and density measurements. Polyaniline salts are used as catalysts for the tetrahydropyranylation of decanol. This process is being reported for the first time. The catalytic use of polyaniline salt is quite practical because of its easy preparation, recovery, and reusability of the catalyst.

Recent advances in the field of electrically conducting polymers have led to a variety of materials with great potential applications. Electrically conducting polymers form a unique class of materials, offering the possibility of controlled electrical conductivity combined with useful processing characteristics, low cost and stability. Among the conducting polymers such as polyacetylene, polyaniline, polypyrrole, polythiophene and polyphenylenevinylene, polyaniline has been most extensively studied, because of its moderately high conductivity upon doping with acids, well behaved electrochemistry, easy preparation, possible processability, good environmental stability and its electrical properties, which can be modified by both the oxidation state of the main chain and protonation.[1,2] Polyaniline is an electrically conducting polymer with features that can be exploited in various applications.[3]

Aniline can be polymerized by chemical or electrochemical methods.[4] In the chemical polymerization method, the synthesis of polyaniline is commonly performed by chemical oxidative (mostly using ammonium persulfate as an oxidizing agent) polymerization of aniline in aqueous[5,6] and emulsion[7,8] polymerization medium. Pron *et al.*[9] have compared the use of different oxidizing agents, such as ammonium persulfate, potassium dichromate, hydrogen peroxide and potassium iodate.

In the literature, mostly water-soluble oxidizing agents such as ammonium persulfate, potassium dichromate, hydrogen peroxide, *etc.*, are used to oxidize aniline to polyaniline salt. Recently, we prepared a polyaniline-sulfosalicylic acid salt in a carrier organic solvent *via* the emulsion polymerization pathway by oxidizing aniline with benzoyl peroxide as the oxidizing agent.[10]

Our current research program is directed towards: (*i*) the first-time preparation of polyaniline salts such as polyaniline-sulfate and polyaniline-nitrate *via* the aqueous polymerization pathway by oxidizing aniline with benzoyl peroxide as an oxidizing agent using a water miscible solvent (water–acetone mixture) and (*ii*) the use of polyaniline salt as catalyst in the tetrahydropyranylation of decanol.

The replacement of current chemical processing with more environmentally benign alternatives is an increasingly attractive subject.[11] The tetrahydropyranyl (THP) group is often the protecting group of choice in peptide,[12] nucleotide,[13] carbohydrate[14] and steroids.[15] The THP group is a versatile protecting group for alcohols and phenols in organic synthesis owing to its stability under strongly alkaline conditions, to Grignard and alkyl lithium reagents, to reduction with inorganic hydrides, and to alkylating and acylating agents, such that the THP group has been widely used for hydroxy protection.[16] In addition to the well known protic and Lewis acids,[17] other reagents and catalysts such as pyridinium *p*-toluenesulfonate,[18] the hydrochloride salt of poly(4-vinyl pyridine),[19] iodotrimethylsilane,[20] triphenyl phosphine hydrobromide,[21] montmorillonite,[22] bis(trimethylsilyl)sulfate,[23] Nafion-H,[24] *etc.*, have been used to effectuate the tetrahydropyranylation of alcohols.

Experimental

Materials

Reagent grade aniline from E. Merck was vacuum distilled under nitrogen prior to use. Benzoyl peroxide was recrystallized from chloroform–methanol. Analar grade (99% pure) reagents such as nitric acid, sulfuric acid, sodium lauryl sulfate (all from BDH, India) and dihydropyran (Fluka) were used as received. All other reagents were used as received.

Preparation of polyaniline salt catalyst. Benzoyl peroxide (4. 85 g) was dissolved in 60 ml acetone. To this solution, 2.0 g sodium lauryl sulfate in 30 ml distilled water was added. Aniline (2.4 ml) in 100 ml aqueous solution containing acid (9 ml sulfuric acid or 13.4 ml nitric acid) was introduced dropwise into the above solution at 40 °C. The mixture was stirred for 8 h at 40 °C and the precipitated polyaniline salt was filtered, washed with 3 L of distilled water, followed by methanol and acetone. The resulting polymer salt was finally dried at 100 °C until a constant mass was reached. The yields of polyaniline salt with protonic acids such as sulfuric acid and nitric acid was 2.05 and 2.01 g, respectively.

Procedure for tetrahydropyranylation. Tetrahydropyranylation of dihydropyran and decanol was carried out in a 10 ml round bottom flask using polyaniline salt as catalyst. The

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reaction mixture was heated at a particular temperature for a particular time (details of the experimental conditions are given in tables). The reaction mixture was filtered and washed with hexane to recover the catalyst. The hexane solvent was evaporated off. The yield of the product was calculated using GC. The product (isolated through column) was analyzed by FT-IR and ^{1}H NMR spectral techniques and the authenticity of the product was established.

Measurements

The Fourier-transform infrared spectrum of the polymer sample (as KBr pellet) was recorded using a Bomem MB 100 FT IR spectrometer in the range 400–4000 cm^{-1}. The X-ray diffraction spectrum of the polymer sample was recorded using D5000 Siemens equipment. The particle size of the polymer powder was determined using a Malvern Mastersizer 2000 by dispersing polymer powder in distilled water. The polymer sample in the form of a pellet was obtained by subjecting the sample to a pressure of 93 MPa. Pellet density was determined from the mass per unit volume of the pressed pellet.

The resistance measurement of the sample was measured at room temperature using the four probe method on a pressed pellet. The pellet was obtained by subjecting the polymer sample to a pressure of 93 MPa. The resistance measurement was carried out using a Keithley Model 220 programmable current source and Keithley Model 195A digital voltmeter. The reproducibility of the result was checked by (*i*) measuring the resistance value thrice for each pellet, (*ii*) measuring the resistance for a batch of three pellets of each sample, and (*iii*) measuring the length and area 5 times. Since the mean value were used in the calculation of resistance, the total error involved is <3%.

Results and discussion

In this paper, the application of polyaniline salt as a catalyst is tested. Polyaniline salts (PANI-H_2SO_4 and PANI-HNO_3) were prepared by chemical oxidative polymerization of aniline using benzoyl peroxide in the presence of acid such as sulfuric or nitric acid.

Yield, conductivity and density

The yield of the polyaniline salts, 83.2 and 82.0% (based on the amount of aniline used in the reaction), was found to be nearly the same with sulfuric and nitric acid, respectively. Similarly, the conductivity of the salts, 0.04 and 0.03 S cm^{-1}, was found to be nearly the same. The density of the polyaniline salts prepared using sulfuric and nitric acid was found to be 1.20 and 1.23 g cm^{-3}, respectively.

Infrared spectra

Generally, similar infrared spectra were observed for the polyaniline salts prepared using sulfuric acid and nitric acid. As a representative system, the infrared spectrum of polyaniline prepared using sulfuric acid is shown in Fig. 1. The vibrational bands observed for polyaniline are reasonably explained on the basis of the normal modes of polyaniline. The band at 3270–3400 cm^{-1} is assigned to the NH stretching vibration of the $-C_6H_4NHC_6H_4-$ group. The one at 2935 cm^{-1} is assigned to the vibration associated with the NH_2^+ part in the $-C_6H_4NH_2^+C_6H_4-$ group. The 1585 and 1490 cm^{-1} bands are due to benzene and/or quinone ring deformations, the 1315 cm^{-1} band is the CN stretch of a secondary aromatic amine, and the 820 cm^{-1} band arises from aromatic CH out-of-plane bending. In the region of 1015–1175 cm^{-1}, aromatic CH in-plane-bending modes are usually observed. For polyaniline, a strong band characteristically appears at 1150 cm^{-1}, which has been explained as an electronic band or a vibrational band of nitrogen quinone. The CH out-of-plane bending mode has been used as a key to identifying the type of substituted benzene. For the polymer salt this mode was observed as a single band at 820 cm^{-1}, which falls in the 800–860 cm^{-1} range reported for a 1,4-substituted benzene. A similar band was observed for the polyaniline salt prepared using ammonium persulfate as the oxidizing agent.[5,25,26]

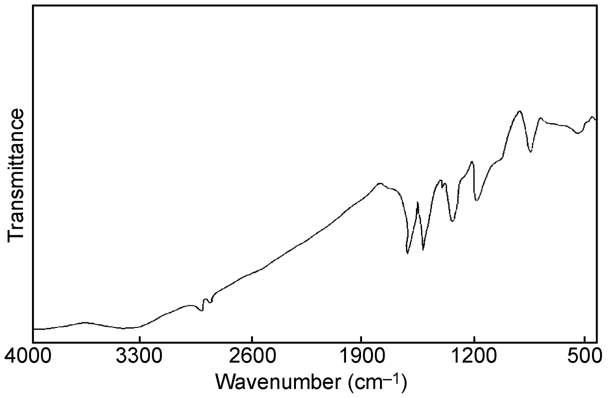


Fig. 1 Infrared spectrum of PANI-H_2SO_4 salt.

X-Ray diffraction spectra and particle size analysis

Generally, a similar X-ray diffraction pattern was observed for the polyaniline salts prepared using sulfuric acid and nitric acid. As a representative system, the X-ray diffraction pattern of polyaniline salt powder prepared using sulfuric acid is shown in Fig. 2. It shows two peaks at around 20 and 25° and this is similar with the value reported in the literature[3] (references therein).

A similar particle size distribution pattern was also observed for the polyaniline salts prepared using sulfuric acid and nitric acid. As a representative system, the particle size distribution of the polyaniline salt powder prepared using sulfuric acid is shown in Fig. 3. The particle sizes of the PANI-H_2SO_4 and PANI-HNO_3 were found to be in the range of 0.3 to 285 μm and 0.5 to 300 μm, respectively.

Tetrahydropyranylation

Polyaniline salts prepared using sulfuric and nitric acid were used as catalysts in tetrahydropyranylation of decanol (Scheme 1). Tetrahydropyranylation of decanol was carried out at 25 °C at different intervals of time using different amounts of PANI-HNO_3 salt catalyst; the results are reported

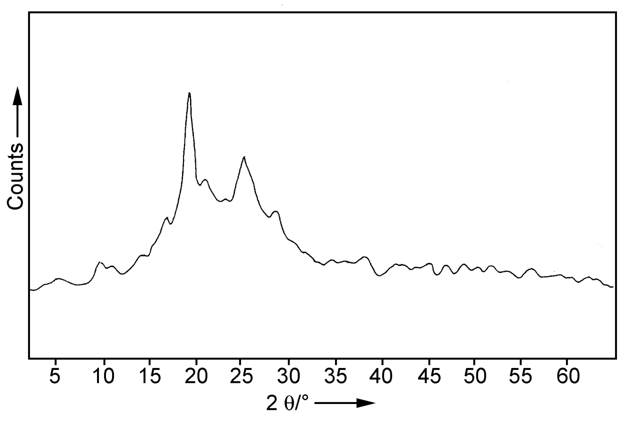


Fig. 2 X-Ray diffraction pattern of PANI-H_2SO_4 salt.

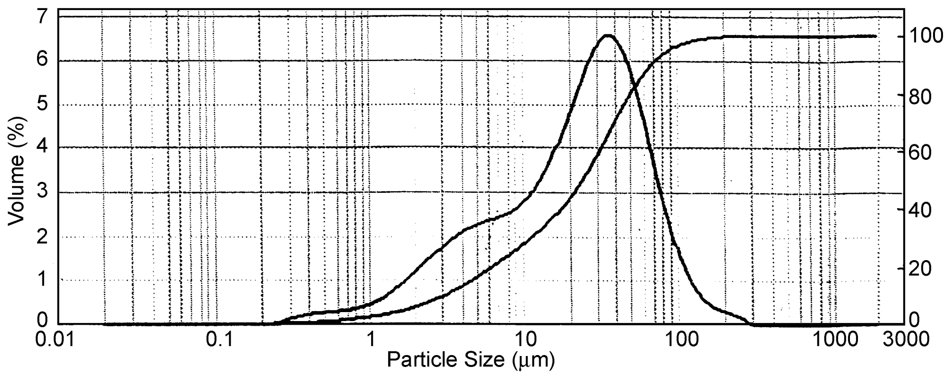
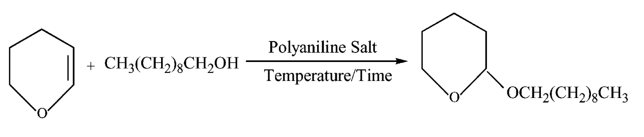


Fig. 3 Particle size distribution of PANI-H_2SO_4 salt.



Scheme 1

in Table 1. The yield of the ether product increased with reaction time and attained a maximum (38%) at 24 h with the use of 10 wt % catalyst. When the amount of catalyst is increased to 15 wt % the maximum yield (52%) was obtained at 20 h. Also, 20 wt % of the catalyst gave 52% product at 20 h. This result shows that 52% of the ether can be obtained using 15 wt % of the catalyst for 20 h.

Tetrahydropyranylation of decanol was carried out at 50 °C at regular intervals of time using 15 wt % of PANI-HNO_3 salt catalyst; the results are reported in Table 2. The yield of the ether product increased with reaction time and attained its maximum yield (52%) at 5 h.

To see the effect of the PANI-H_2SO_4 catalyst, tetrahydropyranylation of decanol was carried out at 25 °C at regular intervals of time using 15 wt % of PANI-H_2SO_4 salt catalyst and the results are included in Table 2. The maximum yield (72%) of the ether product was obtained within one hour. This result shows that PANI-H_2SO_4 gives a better yield compared to PANI-HNO_3 catalyst and this may be due to the higher strength of sulfuric acid.

The reusability of the catalyst was checked by the tetrahydropyranylation of decanol with PANI-H_2SO_4 salt as catalyst at 25 °C for one hour, which resulted in a yield of 72%. Polyaniline salt catalyst was recovered and reused thrice for tetrahydropyranylation of decanol and the ether was obtained in 70–72% yields. After the fourth trial, the catalyst was recovered and characterized by infrared, X-ray diffraction, particle size and density measurements. Similar infrared spectra, X-ray diffraction patterns, particle sizes (0.3–285 and 0.2–270 μm) and density (1.23 and 1.20 g cm^{-3}) of the PANI-H_2SO_4 catalyst were obtained before and after the reaction.

Generally, tetrahydropyranylation of alcohols is carried out by Lewis acids, *p*-toluene sulfonic acid *etc.*, as catalysts. In this work, polyaniline salts of nitric acid or sulfuric acid were tested as polymer supported catalysts. Sulfuric acid or nitric acid in the polymer chain takes part in the THP reaction. The mechanism of the reaction would be similar to the pyridinium *p*-toluenesulfonate promoted tetrahydropyranylation of alcohol.

The tetrahydropyranylation of decanol yielded 72% when carried out at 25 °C for 1 h with PANI-H_2SO_4 as the catalyst. PANI-HNO_3 catalyst yielded 52% product when the reaction was carried out at either 25 °C for 20 h or 50 °C for 5 h. The yields of the product obtained using polyaniline salt catalysts are lower than those of other catalysts reported in the literature; for instance, *p*-toluene sulfonic acid[27] gave 98–100% yield at 25 °C for 1.5 h and pyridinium *p*-toluene sulfonate[18] yielded 94–100% at 20 °C for 4 h.

Conclusion

Polyaniline salts can be prepared using benzoyl peroxide as an oxidizing agent. A mild and versatile THP method has been developed based on polyaniline salts. This method has several advantages: the catalytic use of polyaniline salt is quite practical because of its easy preparation, recovery, reusability, and

Table 1 Tetrahydropyranylation of decanol catalyzed by a polyaniline salt prepared using nitric acid[a]

	Yield of the product (%)[b]		
	Percentage of polyaniline salt used		
Time/h	10%	15%	20%
2	2.6	4.5	25.6
4	3.4	5.6	28.0
10	4.3	10.5	43.1
16	18.2	20.7	50.3
20	34.3	52.1	52.7
24	38.0	51.8	52.4
26	37.8	52.0	52.4

[a] Reaction conditions: 3,4-dihydro-2*H*-pyran (1.0 g), decanol (1.0 g), polyaniline salt (100, 150, 200 mg), temperature (25 °C). [b] Product analyzed by GC.

Table 2 Tetrahydropyranylation of decanol catalyzed by polyaniline salts prepared using nitric acid[a] and sulfuric acid[b]

	Yield of the product (%)[c]	
Time/h	PANI-HNO_3	PANI-H_2SO_4
1	23.6	72.1
2	29.0	71.3
3	39.2	72.6
4	45.9	70.8
5	52.0	72.0
6	51.8	72.2

[a] Reaction conditions: 3,4-dihydro-2*H*-pyran (1.0 g), decanol (1.0 g), PANI-HNO_3 (150 mg), temperature (50 °C). [b] Reaction conditions: 3,4-dihydro-2*H*-pyran (1.0 g), decanol (1.0 g), PANI-H_2SO_4 (150 mg), temperature (25 °C). [c] Product analyzed by GC.

lower toxicity of the catalyst. However, the efficiency of polyaniline salt catalysts in tetrahydropyranylation is found to be low and work is under progress to improve the activity.

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